

## **OIL BEHAVIOUR, FATE AND MODELLING PROJECTS**

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### **ABSTRACT**

The Emergencies Science Division of Environment Canada in Ottawa conducts projects in oil behaviour, fate, and modelling, and currently has eight projects underway related to these topics. The projects are summarized and preliminary results presented.

The projects are: 1. The physics of water-in-oil emulsions - studies conducted to investigate the processes of emulsion formation; 2. Measurements of emulsion stability - assessment and development of analytical techniques to assess water-in-oil emulsion stability; 3. Study of oil evaporation - new results will be presented to describe the physics of oil evaporation and provide prediction equations; 4. Study of natural dispersion - the relation of natural dispersion to parameters such as energy; 5. Development of an oil spill model; 6. Development of fate-specific analytical techniques - chemical techniques are being developed to measure oil fate and behaviour directly; 7. Compilation of an oil properties catalogue and development of physical analytical protocols for crude oils; and 8. Preparation of technical summaries on oil behaviour topics.

### **INTRODUCTION**

Fate and behaviour studies are fundamental to oil spill research and their results are important for operational response. Knowledge of the ultimate fate and behaviour of oil should drive countermeasures decisions. Research is being conducted around the world on oil fate and behaviour. However, the effort has not been focussed as it should have been. Unfortunately, research funding for oil spills is very oscillatory. Fate and behaviour studies require a long, concerted effort to yield valuable results. Because of this, fate and behaviour studies have suffered much more than others from funding 'spurts'. Little research has been maintained at universities because of the lack of sustained funding. Few other research organizations have the facilities, equipment, and expertise to carry out fundamental studies. A second difficulty in the field has been the tendency to fund one-year studies. Typically, little can be answered in a year. Specialized apparatus take 6-12 months to build or to acquire. Little time is left to operate these. The learning curve is also a factor. It is generally accepted that in a specialized field it takes a new scientist six months to produce any useful work, two years to become productive, and five years to be fully productive. Hopefully, future efforts will allow for longer-term studies on fate and behaviour.

The state of the art in the field of fate, behaviour, weathering, and modelling could be summarized as variable. There are many deficiencies in our knowledge about the fate, weathering, and modelling of oil spills.

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The fate, behaviour, and transformation of oil are dominated by the reality that oil is a varying mixture of hundreds of compounds. Many laws of chemistry and physics are inapplicable to oil because they assume ideal liquid or gas behaviour. Much of the knowledge gained by chemists over the years is difficult to apply to the field. Examples of this include even standard physical measurements such as pour point. Strictly speaking, a single pour point value does not exist for a mixture like oil. The current state of the art for pour-point measurement is poor and reproducibility depends largely on the perceptions of the operators, despite very well defined ASTM standards. Oil, strictly speaking, does not have a single boiling point, a melting point, nor an evaporation rate. The components of oil have their own well defined physical parameters, but these are modified and obscured by the bulk behaviour factors. In the place of these 'pure' chemical parameters, we have developed bulk parameters to describe oil properties and behaviour. These have relevance and definition only for mixtures. Examples of these include initial boiling point and percent residuum.

The measurement of oil and petroleum properties is also dominated by the fact that it is a mixture. Almost all measurement standards are developed for petroleum refining, where the important factors relate to distillation properties and not environmental behaviour. There is a pronounced lack of work on measurement techniques and standards as these relate to oil fate and behaviour in the environment. This is most probably a result of the fact that the oil spill and oil pollution industry is small and does not create the demand for specialized measurement techniques.

## RESEARCH IN PROGRESS

### PHYSICS OF EMULSIONS

Environment Canada, in cooperation with the U.S. Minerals Management Service, is conducting a series of studies on emulsions. Study continues on the mechanism of water-in-oil emulsion formation. The literature shows that there is little understanding of the formation of water-in-oil emulsions. Information on the kinetics of formation at sea is less abundant. Emulsion formation is a result of surfactant-like behaviour of the polar and asphaltene compounds. These are similar compounds and both behave like surfactants when they are not in solution. When there are insufficient amounts of aromatic components to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins to stabilize an emulsion is about 3%. This amount requires further verification and may, in fact, depend on the amount of other components present. The asphaltenes and waxes are stabilized in the oil by BTEX (Benzene, Toluene, Ethylbenzene, and Xylenes). After these weather sufficiently, asphaltenes and resins are no longer solubilized and can precipitate to stabilize emulsions. The solubility factor requires further investigation. Emulsions begin to form when the above chemical conditions prevail and when there is sufficient sea energy. This energy is not measurable with current state-of-the-art techniques and its relative amount is not known in terms of emulsion onset. The literature indicates that the relative energy required to form emulsion varies, but is not high. Investigation of the amounts of energy and water droplet sizes remains outstanding - particularly because of lack of accurate measurement techniques.

## EMULSION STABILITY

Emulsion formation is a key complicating factor to oil spill cleanup. The most important question related to emulsions analysis is whether they are stable. In the strict thermodynamic sense, all emulsions are unstable; however, experimental evidence has shown that some emulsions will persist over a matter of weeks. A commonly accepted definition is that an emulsion is considered stable if it persists at least five days at 15°C. An assessment of several tests for stability has been correlated to the basic definition. These tests include: observation of the colour of the emulsion, viscosity, elasticity, zero-shear rate viscosity, water content, and conductivity. The latter two measures are not, in themselves, reliable indicators of emulsion stability. It has been noted that most, if not all, emulsions that are stable are reddish in appearance and those that are not are black. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than two orders-of-magnitude greater than that of the starting oil. The zero-shear-rate viscosity is at least six orders-of-magnitude greater than the starting oil for a stable emulsion. For an unstable emulsion, it is usually less than two or three orders-of-magnitude greater than the viscosity of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. These measures can then be used in the design of any emulsion-breaking test as a quick analytical tool. It should be noted that very few emulsions have questionable stability. The usual situation is that emulsions are obviously either stable or unstable. Analytical techniques are then largely required to test the few questionable emulsions or to rapidly confirm the stability of the others.

Studies in the past year have shown that a class of 'very stable' emulsions exists, characterized by their persistence over several days. These stable emulsions actually undergo an increase in viscosity over time. Monitoring of these emulsions has been performed for over two weeks and new studies over much longer times are being conducted. 'Unstable' emulsions do not show this viscosity increase and their viscosity increases by less than two orders-of-magnitude from the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude. Much more research is needed to confirm these results and also to determine whether there are several stability classes of emulsion.

An ancillary study is the development of several emulsion formation techniques. Several apparatuses have been tested and procedures developed to use these for making emulsion.

## STUDY OF OIL EVAPORATION

This study is conducted by Merv Fingas, as part of PhD thesis requirements at McGill University, Montreal. The objective is to study the fundamental relationships involved in the evaporation of crude oils and to develop an empirical equation for oil evaporation.

An automated methodology has been developed to obtain data. About 90 runs averaging 2 1/2 days have been conducted. The scope of the experimentation to date has included varying the data collection methods and oil thickness.

The findings to date are that simple empirical equations can be developed which accurately predict oil evaporation. There appear to be more fundamental findings on the evaporative behaviour as well. The physical findings are that oil is not specifically boundary-layer regulated. This has profound implications for most oils that are not light or where boundary-layer regulation is not important, including:

1. area of evaporation is not important and can be ignored
2. wind speed is not important and can be ignored
3. after a small initial "burst" of evaporation, most (non-light) oils will evaporate at the same rate governed by their make-up regardless of the environmental conditions, except for temperature

4. temperature is the only environmental consideration

5. evaporation can be predicted for mass loss by an equation of the form:

$$E_v = MT \ln t$$

where:  $E_v$  is the mass evaporating per unit time,  $t$

$M$  is the mass

$T$  is the temperature

$t$  is the time

6. evaporation can be predicted even more simply by an equation of the form:

$$E_v = T \ln t$$

where:  $E_v$  is the percentage evaporating per unit time,  $t$

$T$  is the temperature

$t$  is the time

7. the constant parameters for the above can be calculated accurately from physical properties.

Research continues and will result in methods to predict the evaporation equations from simple relationships from oil properties.

## NATURAL DISPERSION

Some study of the natural dispersion process has been conducted with chemical dispersion studies. Further work is necessary both to understand the process and to predict it with some accuracy. Chemical dispersion, which has been studied more extensively, increases with energy in a linear fashion until a maximum is reached. For light oils, this maximum is about 80%. For heavier oils, this is about 65%. The dispersion curve is very steep, that is only a small amount of energy causes a large amount of change in dispersion. There exists an energy threshold below which little dispersion occurs. Chemical dispersion curves for different oils are parallel (have similar slopes). This may indicate that the mechanism is fixed and only the threshold varies.

Natural dispersion is analogous to chemical dispersion except that the increase with energy is much less. The onset of natural dispersion is difficult to assign but is similar to, or higher than, that of chemical dispersion. In testing done to date, natural dispersion will only rise to about 30% for light oils and about 5% for heavy oils. How this rate relates to time, has not yet been determined.

The major question these experiments raise is how the energy in these tests relates to that at sea. There are a few observations that show that most typical sea energies occur at the low end of the energy range shown in the test data presented here. In one test at sea, ASMB and Bunker C light were observed to start dispersing naturally at a sea state of Beaufort 6. The EKOFISK BRAVO oil was observed to disperse naturally at sea states around Beaufort 5 or 6. It is recognized that turbulent energy is the important factor for dispersion. At this time technology does not exist to measure this type of energy at sea and in the laboratory.

There may be potential for energy measurement in the future with laser doppler or hot wire instruments. This development would ensure that the findings reported in this study could be directly applied to sea surface observations.

#### DEVELOPMENT OF AN OIL SPILL MODEL

A partnership has been formed to fund development of a state-of-the-art oil spill model system.

Partners are:

- (1) Applied Science Associates, Inc.
- (2) Aramco Oil Field Services
- (3) Canadian Petroleum Association
- (4) Chevron Oil Field Research Company
- (5) Environment Canada
- (6) Exxon Production Research Company
- (7) Mobil Research and Development Corporation
- (8) U.S. Army Corps of Engineers

The specific objectives of this project were:

- (1) to summarize advances made over the past decade in oil spill modelling, including the identification of significant assumptions and limitations, and to prepare a detailed model development plan;
- (2) to incorporate recent advances into a modular, interactive oil spill model system, operating on IBM-compatible personal computers, such that alternate algorithms for each process can be interchanged and evaluated;
- (3) to structure the model for broad-scale spill response and contingency planning on a worldwide basis, allowing also for site-specific use;
- (4) to standardize formats for environmental data storage, retrieval, and display within the framework of a geographical information system (GIS), such that partners and their affiliates can readily apply the model and share data on a worldwide basis, as desired.

The main project is completed and an operational version is available. The prime demonstrator area is the Straits of Juan de Fuca. Two subsequent versions have also been issued.

The consortium has been extended into a second phase which will consist of adding several features such as a three-dimensional component, a riverine-linking system, and data import functions.

#### DEVELOPMENT OF A FATE-SPECIFIC ANALYTICAL TECHNIQUES

Weathering The quantitative information of the weathering of spilled oil in the environment is essential to the full understanding of the fate and behaviour of oil in the environment. This data is also useful for spill modelling. The key to acquiring data on oil weathering is the availability of precise and reliable chemical information. Exact quantitation of compounds in the oil can provide this crucial data. In this study, a light crude oil (Alberta Sweet Mix Blend, ASMB) was used to measure the effect of weathering (the oil was evaporated to varying degrees 0% to 45%, w/w) on the chemical composition of the oil on a laboratory scale.

The chemical composition of this oil has been extensively characterized and quantified in our lab. Using GC/FID and GC/MS, the weathering effects of a light crude oil were thoroughly investigated: (1) the complete compositional information on a light crude oil at various degrees of evaporation was obtained; (2) the composition and concentration changes of key components and component groupings in a light crude oil were quantitatively correlated to evaporative loss or weathering degrees of this oil; (3) two opposing effects during evaporation weathering (one is the loss of oil components due to evaporation, and another is build-up of oil components due to volume deduction) were examined; (4) the so-called "pattern recognition" plots involving more than 100 important individual oil components and component grouping were graphically depicted, which would permit deduction of a best set of values for exposure to evaporative weathering; (5) a "weathering index" concept was proposed to quantify weathering degree of oil with the short-term weathering processes being dominated by evaporation; (6) relatively simple and very useful mathematical equations were developed. The equations and data can be utilized to describe the weathering behaviour of oil and to estimate the evaporation extent of oil.

**Biodegradation** A "complete chemical analysis method for biodegradation oil product by GC/MS and GC/FID" was developed. The analytes include biodegradable saturate compounds (n-alkanes and isoprenoids), polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (alkyl groups from C1 to C4), and highly biodegradation-resistant biomarker compounds (triterpanes and steranes). So far, several hundred biodegradation oil samples have been analyzed. For each sample, three analyses (one by GC/FID and two by GC/MS) were performed for its fraction 1 (F1) to determine the concentration of the total saturates and to quantify the distributions of n-alkanes and biomarker compounds; two analyses using GC/MS for the fraction 2 (F2) to quantify the target PAHs and their homologues; one run for the fraction 3 (F3, the combined fraction of F1 and F2) by GC/FID to determine the total petroleum hydrocarbon (TPH) value.

**General Methods** In recent years, the Emergencies Science Division (ESD) of Environment Canada has conducted projects to investigate various countermeasures in responding to oil spills. One of the important elements in these projects is to develop quantitative oil analytical methods. The proposed method relies on the use of a 3-gram micro silica gel column to fractionate oil into saturated, aromatic, and polar fractions, and then the use of GC/FID and GC/MS to identify, characterize, and quantify the important oil components and component classes (such as n-alkanes from n-C8 to n-C40 and isoprenoids, PAHs and their alkylated homologues, and biomarker triterpane and sterane compounds). Using this method, over 280 compounds in a light crude oil have been positively identified; 22-year-old Arrow oil samples have been unambiguously characterized through the quantitative comparison of the unique and sensitive distribution pattern of biomarker compounds with the source oil; the effect of weathering on the chemical composition of oil has been quantitatively understood through the "pattern recognition" plots involving 100 oil-specific individual components and component groupings; and screening procedures have been developed for assessing the efficacy and toxicity of oil spill bioremediation agents by analyzing hundreds of biodegradation oil samples.

The proposed analytical methods for oils are more selective and representative of the true composition of oil, and hence more defensible than traditional methods which were originally designed for industrial waste and hazardous waste.

## OIL CATALOGUE AND DEVELOPMENT OF NEW MEASUREMENT TECHNIQUES

The oil properties catalogue was first compiled by Environment Canada in 1984. The United States Minerals Management Service has jointly funded the catalogue program since 1989. The catalogue was started to provide physical and chemical data relevant to oil spills. No catalogue of this type existed and data were found only by random searching of the literature. Compilation of the existing data for the first catalogue showed that very few data existed.

The catalogue has been immensely popular because it satisfies a need that had not previously been recognized. There continues to be a demand both for data on oils not already in the catalogue and for more data types. To this end, a 1992 edition of the catalogue was published in 1993 which is also available on diskette and through SPILLS, an on-line electronic bulletin board.

Substantial improvements have been made to the data entry and other programs which operate on the oil database. It is now possible to produce a text file of all the data for any oil or all the data for any physical property, e.g. viscosity. These text files can be easily imported into spreadsheet programs for easy data manipulation.

Several innovations and new measurements have been introduced. Surface and interfacial tensions are now measured using a Kruss K 10 ST digital tensiometer. This instrument makes the measurements automatically. This has allowed faster sample throughput. Accuracy and reproducibility are also improved.

New analytical techniques are being developed and added as time proceeds. Simulated distillation (ASTM D 2887) can now be performed on those oil products that have boiling ranges between 90°C and 538°C. Emulsion viscosities are now measured for all stable emulsions. A new protocol has been developed for weathering oils using rotary evaporation at ambient pressure, with air flow and mild (80°C) heating. This new method will produce a weathering curve and equation specific to each oil. Oils will also be weathered gradually (three or four different points on the curve) and complete analyses will be done on the weathered oils.

Future work related to the oil properties catalogue will include the development of new or improved protocols for hydrocarbon group analysis, chemical dispersibility, emulsion formation and stability, and total oil analysis by GC/MS. Better (more useful) equations relating physical-chemical properties to weathering at sea will also be developed. In the future, data will be added on common industrial and domestic oil products. Representative samples of these will also be analyzed in-house. Quality assurance procedures for all analyses done in-house are currently under review.

The first technique under development is that of group analysis. Oils can be fractionated into different hydrocarbon groups on the basis of solubility and adsorption characteristics. A common protocol consisting of a sequence of separations using dilute solutions in appropriate solvents and adsorption columns is known by the acronym SARA: saturates, aromatics, resins, asphaltenes.

These group designations are indirect labels in terms of chemical composition. The saturates fraction is the most descriptive because it contains only aliphatic compounds. The aromatics contain a variety of aromatic compounds, some with saturated groups attached. The resins are higher in heteroatoms and have a higher concentration of aromatic carbon. The asphaltenes are the highest molecular weight fraction and contain most of the polar compounds. The distinctions between aromatics and resins, and between resins and asphaltenes, therefore are

not clear. For all of these fractions, the definition of the separated material is a blend of chemistry and technique. Each group is defined mainly by the procedures followed in its isolation. For example, asphaltene precipitated from n-pentane are not the same as asphaltene precipitated from n-heptane.

In spite of these vagaries, hydrocarbon group analysis may prove to correlate usefully with other oil properties such as chemical dispersibility or emulsion formation tendency and stability.

The original methods for preparing these fractions involved simple precipitation and chromatography on large open columns at low pressure. More recent adaptations of this analysis include high-performance liquid chromatography (HPLC) using high-pressure columns and automated chromatography and detection using silica rods and flame ionization detection (Iatroscan). The problem with the former method is quantitative detection of the complex fractions as they elute from the analytical column.

The Iatroscan method has become increasingly popular and is under consideration as a replacement technique. The main problem with this method is that it is limited to oils with initial boiling points greater than 250°C. This would limit its use to certain oil products and to weathered crude oils which have lost all their low-boiling components. Fresh crude oils will likely have to be analyzed using a combination of techniques, perhaps including a GC analysis of the low boiling components and Iatroscan of the remainder.

#### BOSS - Behaviour of Oil Spills - SUMMARY STUDIES

The BOSS project is a project designed to provide a comprehensive collection and review of data and concepts related to oil spill behaviour. Topics include behaviour of oil spilled at sea but will also include the lesser documented topics of oil on land, on freshwater, and oil in ground. The initial topics chosen for the project include:

1. evaporation
2. water-in-oil emulsification
3. dissolution
4. natural dispersion
5. sedimentation
6. chemical dispersion (only as it affects oil fate and properties)
7. shoreline adhesion
8. spreading
9. drift with wind and coriolis affect
10. biodegradation (only as it affects oil properties and behaviour)
11. submergence and over-washing
12. photooxidation and photolysis

Behaviour and fate in specific situations

13. oil with ice
  - oil under ice
  - oil amongst ice
  - oil in ice
  - oil under or with snow but on ice
14. oil with or under snow



- 15. oil on land
- 16. oil in soil
- Ancillary Topics
- 17. oil analysis summary

The literature in each topic is collected, reviewed, and analyzed in detail. Summaries are prepared and reviewed. These literature summaries are intended to be comprehensive so that the original literature is not required for further applications. Critiques of each paper are prepared.

The first summary is the oil-in-ice topic. Another version of the 'Oil-In-Ice BOSS' has been prepared and is approximately 800 pages in length.

Literature collection on all topics goes on. Over 3900 papers have been collected to date. Work is continuing on preparation of sections on evaporation and emulsification.

#### CONCLUDING REMARKS

Oil behaviour and property work is very important to the understanding of fate and effects in the environment as well as for the design of effective countermeasures. The field, however, is not well studied and has not been funded to the extent necessary. Fate and behaviour studies seem to be particularly vulnerable to the vagaries of funding cycles.

Environment Canada and the United States Minerals Management Service have devoted funds and staff to this area and have made significant progress. Much remains to be learned about oil spills behaviour, and significant scope for research remains.

